Crag Herbicide I*

Analyte:	Crag Herbicide I	Method No.:	S356
Matrix:	Air	Range:	5-27 mg/cu m
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$):	0.053
Procedure:	Filter collection, deionized water extraction, complexation, colorimetry	Validation Date:	12/22/78

1. Synopsis

A known volume of air is drawn through a mixed cellulose ester membrane filter to collect Crag herbicide.

1.2 Crag herbicide is extracted from the filter with 10 mL of deionized water. An aliquot of the extracted sample is mixed with methylene blue to form a colored complex. The sample is then extracted with chloroform and analyzed using a spectrophotometer at 650 nm.

2. Working Range, Sensitivity, and Detection Limit

This method was validated over the range of 5-27 mg/cu m at an atmospheric temperature of 23°C and pressure of 761 mm Hg, using 90-liter samples. For this sample size, the working range is estimated to be 1.5-45 mg/cu m. The upper limit of the range of the method is dependent on the capacity of the mixed cellulose ester membrane filter. The lower limit of the range may be extended by taking larger aliquots of the extracted sample solution for analysis and/or using longer path length spectrophotometer cells.

2.2 The sensitivity of the method can be defined as the slope of the calibration curve. The curve was linear over the range tested. For the validation study a response of 0.474 absorbance units was obtained for an extracted sample containing 100 micrograms/mL Crag herbicide in a 1-cm path length cell.

The detection limit of the analytical method is estimated to be 24 micrograms per sample filter.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in

* Sodium-2,4-dichlorophenoxyethyl sulfate

the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Organic sulfates, sulfonates, carboxylates, phosphates, and phenols complex methylene blue and would be a positive interference. In addition, inorganic cyanates, chlorides, nitrates, and thiocyanates form ion pairs with methylene blue and cause a positive interference Organic materials, especially amines, which compete with methylene blue in the reaction, can cause low results.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 5-27 mg/cu m was 0.053. This value corresponds to a standard deviation of 0.80 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2

4.2 In validation experiments, this method was found to be capable of coming within $\pm$25% of the "true value" on the average 95% of the time over the validation range. The analytical method recovery was determined to be 1.010 for a collector loading of 0.594 mg. In storage stability studies, the mean of samples analyzed after 7 days were within 4.9% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 Collected samples are analyzed by means of a quick, instrumental method.

The collection device is small, portable and involves no liquids

The precision of the method is limited by the reproducibility of the pressure drop across the filter. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter only. Overloading the filter can cause the flow rate to decrease.

6. Apparatus

Filter Unit. The filter unit consists of a 37-mm diameter , 0.8 micrometer pore size mixed cellulose ester membrane filter (Millipore Type AA or equivalent) and a 37-mm polystyrene two-piece cassette filter holder. The filter is held in the two-piece holder, supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.

Manometer.

Thermometer.

Spectrophotometer capable of measurements at 650 nm.

Matched glass cells or cuvettes: 1-cm path length.

Separatory Funnels: 125 mL.

Tweezers.

Scintillation Vials: 20 mL with Teflon-lined caps or equivalent

6.10 Volumetric Flasks: Convenient sizes for preparing standard solutions.

6.11 Volumetric Pipets: Convenient sizes for preparing standard solutions.

6.12 Graduated Cylinder: 50 mL.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Crag herbicide.

Crag Herbicide Stock Solution (1.35 mg/mL). Dissolve 135 mg of Crag herbicide in approximately 50 mL of water. Transfer to a 100-mL volumetric flask and bring to volume.

Distilled water.

Chloroform.

Methylene blue chloride.

Methylene Blue Chloride Solution. Add 0.05 $\pm$ 0.005 g methylene blue chloride to about 250 mL of distilled water into a 1-liter volumetric flask. Slowly add 10 mL sulfuric acid to the flask and mix the resulting solution. Add 50 $\pm$ 0.1 g anhydrous sodium sulfate with enough water to make the total volume in the flask approximately 900 mL. Allow the solution to reach room temperature, and make to volume with water.

7.7 Sodium sulfate, anhydrous.

7.8 Sulfuric acid.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be washed in chromic acid solution and thoroughly rinsed with distilled water and dried. Note: If detergents are used for cleaning glassware it should be noted that any detergent residue left on the glassware may cause a positive interference.

Collection and Shipping of Samples

8.2.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

8.2.2 Remove the cassette plugs and attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing.

8.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.4 A sample size of 90 liters is recommended. Sample at a known flow rate of 1.0-1.5 liters/minute. The flow rate should be known with an accuracy of 5%.

8.2.5 Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.2.6 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.2.7 Remove the filter from the cassette filter holder with clean tweezers and place it into a 20-mL scintillation vial.

8.2.8 With each batch or partial batch of ten samples, submit a blank filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as the blank.

8.2.9 The vials should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. Never transport, mail, or ship the bulk sample in the same container as the sample or blank filter.

Analysis of Samples

8.3.1 Each sample is analyzed separately.

8.3.2 Pipet 10 mL of water into each vial. Swirl the contents in each vial occasionally for a period of 15 minutes.

8.3.3 Appropriate filter blanks must be analyzed at the same time as the samples.

8.3.4 Add 50 mL of chloroform and 25 mL of the methylene blue chloride solution to a 125-mL separatory funnel.

8.3.5 Add an aliquot of 1 mL of the extracted sample solution to the separatory funnel.

8.3.6 Stopper the separatory funnel and vent. Shake continuously for 2 minutes, venting occasionally.

8.3.7 Set the separatory funnel upright for 15 minutes. Remove the bottom chloroform layer into a clean flask.

8.3.8 Prepare a blank using the same procedure described above, except that 1 mL of water is used instead of the sample.

8.3.9 Read the absorbance of the chloroform layer through a 1-cm cell at 650 nm against the blank.

9. Calibration and Standardization

9.1 A series of standards varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study is prepared and analyzed under the same conditions as the unknown samples. Curves are established by plotting concentration of Crag herbicide in mg/10 mL versus absorbance.

From the stock solution (Section 7.2) appropriate aliquots are withdrawn and dilutions are made in water. Prepare at least 4 standards to cover the range of 0.13-4 mg/10 mL. This range is based upon a 90-liter sample.

9.3 Add 50 mL of chloroform and 25 mL of the methylene blue chloride solution to a separatory funnel.

Add 1 mL of standard into the separatory funnel, and continue the procedure described in Sections 8.3.6-8.3.9.

9.5 Prepare a standard calibration curve by plotting mg/10 mL versus absorbance.

10. Calculations

10.1 Read the weight, in mg, corresponding to each absorbance reading from the standard curve. No volume correction is needed, because the standard curve is based on mg/10 mL deionized water.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} \quad \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in blank filter

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of Crag herbicide in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Crag Herbicide, prepared under NIOSH Contract No. 210-76-0123.